Stokes Parameters and Rovibrationally Resolved Cross Sections for the $X^1\Sigma_g^+(v=0,N=1) \rightarrow d^3\Pi_u^-(v=0,N=1)$ Excitation in H_2

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We report for the first time the calculation of Stokes parameters and state-to-state rovibrationally resolved differential cross sections for the excitation $X^1\Sigma_g^+(v=0,N=1) \rightarrow d^3\Pi_u^-(v=0,N=1)$ in H_2 by electron impact at 25 eV. Comparison with the only available experimental data is encouraging.

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In the last two decades there have been considerable experimental and theoretical efforts devoted to a better understanding of the dynamics of electron-impact excitation of *atoms* with the help of coherence and correlation parameters (CCP) [1–4]. The CCP can be measured in electron-photon coincidence experiments, where the emitted radiation from a specially selected ensemble of atoms or molecules is observed, namely, from those atoms or molecules that scattered the electrons into a well defined direction with a well defined energy loss [1,4]. Such an ensemble in general can be characterized by an alignment tensor ("an electric quadrupole moment" of its charge distribution) and by an orientation vector ("a magnetic dipole moment" describing its internal dynamical state) [1–4]. These features of the radiating ensemble of atoms or molecules manifest themselves in the intensity and polarization characteristics of the emitted radiation, quantitatively in the values of the measured Stokes parameters [1–4]. The comparison of CCP with theory is done at the level of complex excitation amplitudes and their interference, rather than at that of the usual excitation cross sections. Thus, while providing detailed information on the target state immediately after the collision, the CCP constitute a most sensitive test to theoretical models and approximations. Although the basic theoretical framework for the interpretation of an electron-photon coincidence experiment for *molecules* was laid down by Blum and Jakubowicz (BJ) in 1978 [5], its application is still very limited, since only a few such experiments have so far been reported [6–10]. McConkey *et al.* [9] demonstrated the feasibility of an electron-photon coincidence experiment involving rotationally resolved levels, and have reported Stokes parameters for the excitation of the $d^3\Pi_u^-(v=0,N=1)$ level of H_2. In addition, rovibrationally resolved relative integral cross sections have been measured recently by Ottinger and Rox [11] for the excitation of the $c^3\Pi_u^-(v=0,1,2,3,N=2)$ levels of H_2. On the theoretical side, however, no calculated CCP have ever been reported for molecules.

In this Letter we report, for the first time, theoretical results for Stokes parameters and rovibrationally resolved differential cross sections (DCS) of a molecule. Specifically, we considered the electron-impact excitation of the $d^3\Pi_u^-(v_1=0,N_1=1)$ level of H_2 from the $X^1\Sigma_g^+(v_0=0,N_0=1)$ level at the incident energy $E_0 = 25$ eV , where our theoretical results can be compared with the experimental data of McConkey *et al.* [9].

In what follows, we give a brief description of the formalism used, following BJ's notation: Λ will denote the component of the electronic angular momentum along the molecular axis, S the molecular spin (with component M_S), N the total angular momentum (with component M_N) of the molecule, v will refer to the vibrational quantum number, and n to all other quantum numbers. The subscripts 0 and 1 in these quantum numbers will refer to the initial and excited state of the collision process, respectively. Following BJ, we shall describe the relevant states of H_2 via the Hund's case (b) coupling scheme and we shall use for the molecular states the uncoupled representation $|\Gamma\rangle = |nv\Lambda S M_S N M_N\rangle$. If the electron scattering amplitude for the $\Gamma_0 \rightarrow \Gamma_1$ process is denoted by $f_{\Gamma_1\Gamma_0}$, the radiating system will be described by the wave function $|\Psi\rangle = \sum_{M_{S_1}M_{N_1}} f_{\Gamma_1\Gamma_0}|\Gamma_1\rangle$, assuming that the $|\Gamma_1\rangle$ states with different M_{S_1} and M_{N_1} values are degenerate. In our case, however, due to the possibility of various values for M_{N_0} (for which an isotropic distribution is assumed), the initial molecular state cannot be prepared in a given $|\Gamma_0\rangle$ state. Thus the initial molecu-

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lar state is a mixed (partially coherent) state and then it must be described by a density operator (or density matrix) in the form

$$\hat{\rho}_0 = \frac{1}{2N_0+1} \sum_{M_{N_0}} |\Gamma_0\rangle\langle\Gamma_0|. \quad (1)$$

As a result of the partially coherent nature of the initial molecular state, as well as of the unpolarized nature of the incident electron beam, the excited state will also be partially coherent, being described by the density operator:

$$\hat{\rho}_1 = \frac{1}{2(2N_0+1)} \sum_{M_{N_0} M_{N_1} M'_{N_1} m_0} f_{\Gamma_1\Gamma_0} f^*_{\Gamma'_1\Gamma_0} |\Gamma_1\rangle\langle\Gamma'_1|, \quad (2)$$

with m_0 referring to the spin projection of the incident electron. Instead of describing the radiating state by the abstract density operator, it is convenient to describe it [1–4] by the average values of a set of tensorial operators $T(1)_{KQ}$ $(K = 0, 1, 2; -K \le Q \le K)$ in that state. These average values $\langle T(1)_{KQ}\rangle$ are called state multipoles. $\langle T(1)_{00}\rangle$ is proportional to the rovibrational DCS; $\langle T(1)_{1Q}\rangle$ are proportional to the spherical components of the orientation vector which in turn can be defined as the average total angular momentum $\langle N_Q\rangle$; and $\langle T(1)_{2Q}\rangle$ are proportional to the spherical components of the alignment tensor. In our case these quantities can be given by the formula [5, 9]

$$\langle T(1)_{KQ}\rangle = \mathrm{Tr}(\hat{\rho}_1 T(1)_{KQ}) = \frac{1}{3} \sum_{M_{N'_1} M_{N_1} M_{N_0}} f_{1M_{N_1}1M_{N_0}} f^*_{1M_{N_1}1M_{N_0}} (-1)^{1+K+Q-M_{N_1}} \times (2K+1)^{1/2} \begin{pmatrix} 1 & 1 & K \\ -M_{N_1} & M_{N'_1} & Q \end{pmatrix}, \quad (3)$$

where $f_{N_1 M_{N_1} N_0 M_{N_0}}$ refers to the scattering amplitude of the excitation process, and we have used $N_1 = N'_1 = N_0 = 1$. These state multipoles describe the excited state immediately after the collision and can be directly related to the Stokes parameters which characterize the emitted radiation. However, while the excitation process is fast (collision time $\sim 10^{-16}$ sec) compared with the fine-structure and hyperfine structure relaxation times ($\sim 10^{-14}$ and 10^{-13} sec, respectively), the light emission (lifetime $\sim 10^{-8}$ sec) is not. Then, before the molecule decays, the spin-orbit coupling and nuclear spin coupling effects should be considered, resulting in a time dependence (a "beating") of the state multipoles. If the resolution time of the photon detector is much larger than the radiative lifetime of the fine and hyperfine levels (which was assumed to be the case in the experiment of McConkey *et al.* [9]), the observed signal will be a time average of those quantities. A detailed analysis of these relaxation processes was presented in Refs. [5,9], with the following results for the observed Stokes parameters η_i $(i = 1, 2, 3)$:

$$\eta_1 = -0.058\langle T(1)_{21}\rangle/D, \quad (4)$$

$$\eta_2 = -0.188i\langle T(1)_{11}\rangle/D, \quad (5)$$

$$\eta_3 = 0.029[\sqrt{3/4}\langle T(1)_{20}\rangle - \langle T(1)_{22}\rangle]/D, \quad (6)$$

where $D = 0.555\langle T(1)_{00}\rangle + 0.029\langle T(1)_{22}\rangle + 0.012\langle T(1)_{20}\rangle$.

The diagonal elements of $\hat{\rho}_1$ give the state-to-state rovibronic DCS for the excitation of the M_{N_1} rotational sublevel which in the present case can be written as

$$\sigma_{M_{N_1}}(\theta) = \frac{k_1}{6k_0} \sum_{M_{N_0}} |f_{1M_{N_1}1M_{N_0}}(\theta)|^2. \quad (7)$$

In the adiabatic-nuclei framework the scattering amplitude can be written in the form [12,13]

$$f_{N_1 M_{N_1} N_0 M_{N_0}} = \langle v_1 \Lambda_1 N_1 M_{N_1} \mid f_{\mathrm{el}}(\mathbf{k}_0, \mathbf{k}_1; \mathbf{R}) \mid v_0 \Lambda_0 N_0 M_{N_0}\rangle, \quad (8)$$

where $f_{\mathrm{el}}(\mathbf{k}_0, \mathbf{k}_1; \mathbf{R})$ is the fixed-nuclei electronic scattering amplitude, $\mathbf{k}_0(\mathbf{k}_1)$ is the momentum of the incident (scattered) electron, and $R = \mid \mathbf{R} \mid$ is a given internuclear distance. In order to obtain the amplitudes $f_{N_1 M_{N_1} N_0 M_{N_0}}$ we have calculated $f_{\mathrm{el}}(\mathbf{k}_0, \mathbf{k}_1; \mathbf{R})$ using the distorted wave approximation (DWA) [13,14]. The DWA has been applied successfully to calculate DCS and Stokes parameters for electron-impact excitations of a variety of atoms [1,2,15]. For molecules, although computationally much simpler than the available multichannel theoretical methods, the DWA has been shown [14] to give essentially identical numerical results to the Schwinger multichannel method at the two-state level of approximation even at incident energies a few eV above the excitation threshold. The simplicity of the DWA makes rovibronic excitation studies computationally feasible and thus it is suitable as a first theoretical approach for these processes. Recently, we have used this approximation to calculate the vibrationally resolved DCS for the excitation $X^1\Sigma_g^+(v = 0, N = 1) \rightarrow d^3\Pi_u^-(v = 0, 1, 2, 3)$ [16], and rovibrationally resolved integral cross sections for the excitation $X^1\Sigma_g^+(v = 0, N = 1) \rightarrow c^3\Pi_u^-(v = 0, 1, 2, 3, N = 2)$ in H_2 [17] by electron impact. The numerical procedure and details of the present DWA calculation are essentially the same as in Ref. [16] except for some improvements in the basis set used. For the rotational wave functions in Eq. (8) we used a linear combination of symmetric top wave functions appropriate for ortho-H_2 [18].

After performing the integrations in Eq. (8) we have

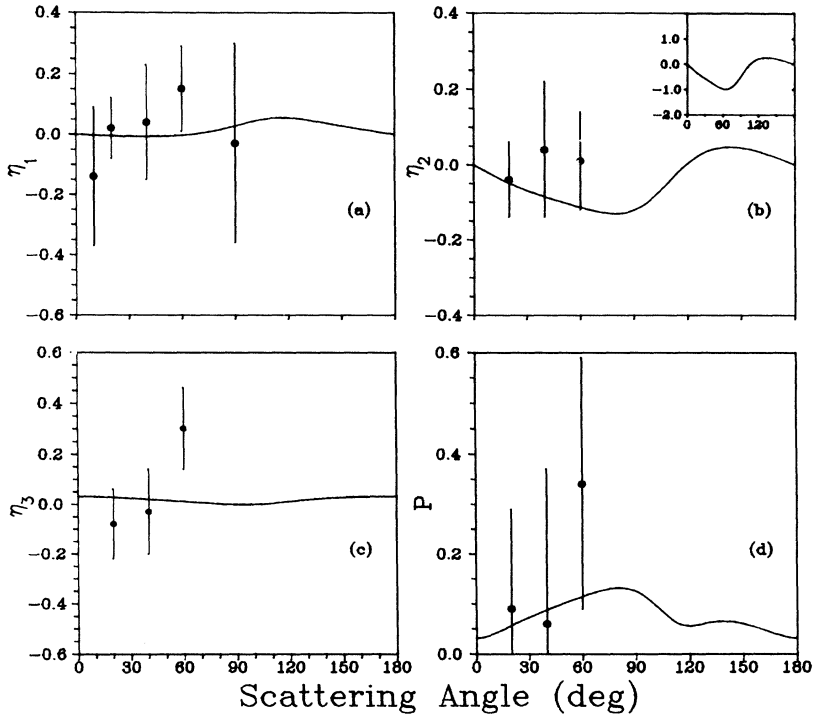

FIG. 1. Stokes parameters η_1, η_2, and η_3 (a)–(c) and polarization (d) for the state $d^3\Pi_u^-(v=0, N=1)$ of H_2 excited electron impact at 25 eV. Solid line, present results; dots with error bars, experimental data from Ref. [9]. The inset in (b) is the Stokes parameter P_3 for the 3^3P state of He [19] (see text).

obtained an expression for the scattering amplitudes $f_{N_1 M_{N_1} N_0 M_{N_0}}$ in terms of the $\langle v \mid T_{lm,l_0 m_0}(R) \mid v_0 \rangle$ matrix elements, where $T_{lm,l_0 m_0}(R)$ are the partial-wave components of the electronic DW-transition matrix defined in Eqs. (13) and (14) of Ref. [13].

Figures 1(a)–1(d) show the calculated Stokes parameters and polarization [i.e., the magnitude of the vector (η_1, η_2, η_3)], along with the experimental data of McConkey *et al.* [9]. The calculated Stokes parameters are small, and are in general agreement with the measured values, within the experimental uncertainty. This smallness is mainly due to fine and hyperfine structure "beating" effects, which are known [4] to reduce significantly the angular anisotropy and the polarizations of the emitted radiation. The experimental values of η_2 [Fig. 1(b)] are very small in the covered angular region. Indeed, McConkey *et al.* [9] speculated that $\eta_2 \simeq 0$ for all angles could be a result of a more fundamental property of the exchange scattering process. However, our calculation shows that η_2 is small but not zero, indicating that a net transfer of angular momentum perpendicular to the scattering plane can occur even in the case of a pure exchange excitation. This analysis reinforces the conclusion of Cartwright and Csanak [19] for the transitions $1^1S \rightarrow n^3P (n = 2-8)$ in the He atom. Also, as observed for rare gases, the net transfer of angular momentum is positive for small scattering angles. In fact, there is a striking similarity in shape between our η_2 results and the corresponding values for the 3^3P state of helium [see inset in Fig. 1(b)]. For forward scattering η_3 gives the pseudothreshold polarization [20]. Our calculated pseudothreshold polarization [Fig. 1(c)] is 3.1%, which is nearly the same magnitude as those reported previously by McConkey *et al.* (1.5% [21] and 2.5% [9]).

In Fig. 2 we show the magnetic-sublevel-specific rovibrationally resolved and total (summed over magnetic sublevels) differential cross sections for the excitation $X^1\Sigma_g^+(v_0=0, N_0=1) \rightarrow d^3\Pi_u^-(v=0, N=1)$ of H_2 for $E_0 = 25$ eV. Unfortunately, there are no experimental data to compare with. An interesting feature is that the forward and backward DCS for magnetic sublevel with $M_{N_0} = 0$ vanish. The same behavior is observed for the $^1S \rightarrow n^1P$ excitations in the helium atom, but for the magnetic sublevel $M_L = 1$ [22]. This can be easily understood in terms of symmetry considerations [23] combined with angular momentum conservation laws. It is interesting to compare the present DCS for the excitation of the $d^3\Pi_u^-$ of H_2 with those of the $^1S \rightarrow n^3P$ transition of helium. The DCS for He (for an incident energy of 40.1 eV) shown in the inset were calculated using first-order many-body theory [24]. Again, remarkable qualitative similarity is observed.

Both the scarceness and the large inaccuracy of the experimental data severely limit their comparison with the

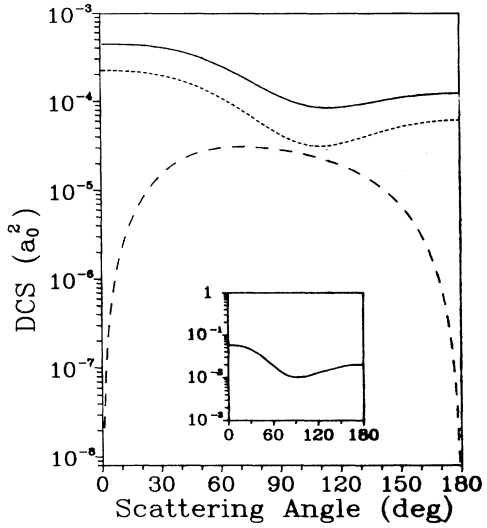

FIG. 2. Rovibrationally resolved DCS for the excitation $X^1\Sigma_g^+(v = 0, N = 1) \rightarrow d^3\Pi_u^-(v = 0, N = 1)$ of H_2 by electron impact at 25 eV. Long-dashed line, present results for the magnetic sublevel $M_{N_1} = 0$; short-dashed line, same for the magnetic sublevel $M_{N_1} = 1$; solid line, same for the total (summed over magnetic sublevel) DCS. Inset: DCS for the 3^3P excitation of He at 40.1 eV [24] (see text).

present results. However, since 1988, significant progress has been achieved in the understanding of how instrumental and other effects can influence the experimental determination of coherence and correlation parameters ([2] and references therein). This has enabled a detailed, quantitative, and comprehensive comparison between atomic experimental data and theoretical predictions. It is hoped that such developments will be applied also for coincidence experiments with molecular targets in the near future, then allowing for more consistent tests of our and other possible future theoretical predictions.

In summary, we have applied the density matrix formalism and the DWA to calculate, for the first time, the Stokes parameters and state-to-state rovibrationally resolved differential cross sections for a molecule. The smallness of our calculated Stokes parameters reinforces the pioneering experimental findings of McConkey *et al.* [9]. Unfortunately, there are not yet enough experimental results that could provide a more consistent analysis.

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